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(21) International Application Number: PCT/GB99/01754 (22) International Filing Date: 3 June 1999 (03.06.99) (30) Priority Data: 9812457.1 10 June 1998 (10.06.98) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation and Research Agency, Ively Road, Farnborough, Hampshire GU14 0XL (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BADYAL, Jas, Pal, Singh [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). WILLIS, Colin, Robert [GB/GB]; CBDE Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBDE Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). COULSON, Stephen, Richard [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). (74) Agent: BOWDERY, A., O.; D/IPR, Formalities Section, Poplar 2, MOD Abbey Wood # 19, Bristol BS34 8JH (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: SURFACE COATINGS			
(57) Abstract <p>A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising one or more organic monomeric compounds, at least one of which comprises two carbon-carbon double bonds, so as to form a layer of cross-linked polymer on said surface. Suitable organic compounds include compounds of formula (I) where R¹, R², R³, R⁴, R⁵, and R⁶ are all independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group. The method is suitable for applying oil and/or water repellent coatings onto substrates such as fabrics.</p> <div style="text-align: center;"> <p>(I)</p> </div>			

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Surface Coatings

The present invention relates to the coating of surfaces, in particular to the production of oil- and water- repellent surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of surfaces are in widespread use. For example, it may be desirable to impart such properties to solid surfaces, such as metal, glass, ceramics, paper, polymers etc. in order to improve preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics, in particular for outdoor clothing applications, sportswear, leisurewear and in military applications. Their treatments generally require the incorporation of a fluoropolymer into or more particularly, fixed onto the surface of the clothing fabric. The degree of oil and water repellency is a function of the number and length of fluorocarbon groups or moieties that can be fitted into the available space. The greater the concentration of such moieties, the greater the repellency of the finish.

In addition however, the polymeric compounds must be able to form durable bonds with the substrate. Oil- and water- repellent textile treatments are generally based on fluoropolymers that are applied to fabric in the form of an aqueous emulsion. The fabric remains breathable and permeable to air since the treatment simply coats the fibres with a very thin, liquid-repellent film. In order to make these finishes durable, they are sometimes co-applied with cross-linking resins that bind the fluoropolymer treatment to fibres. Whilst good levels of durability towards

laundrying and dry-cleaning can be achieved in this way, the cross-linking resins can seriously damage cellulosic fibres and reduce the mechanical strength of the material. Chemical methods for producing oil- and water-repellent
5 textiles are disclosed for example in WO 97/13024 and British patent No 1,102,903 or M. Lewin et al., 'Handbook of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2.

10 Plasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces. This technique is recognised as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. Using this method,
15 plasmas are generated from small organic molecules, which are subjected to an ionising electrical field under low pressure conditions. When this is done in the presence of a substrate, the ions, radicals and excited molecules of the compound in the plasma polymerise in the gas phase and react
20 with a growing polymer film on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex.

25 The success or otherwise of plasma polymerisation depends upon a number of factors, including the nature of the organic compound. Reactive oxygen containing compounds such as maleic anhydride, has previously been subjected to plasma
30 polymerisation (Chem. Mater. Vol. 8, 1, 1996).

US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart liquid repellent properties by

subjecting the surfaces to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane.

However, plasma polymerisation of the desirable oil and
5 water repellent fluorocarbons have proved more difficult to achieve. It has been reported that cyclic fluorocarbons undergo plasma polymerisation more readily than their acyclic counterparts (H. Yasuda et al., J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2411). The plasma polymerization
10 of trifluoromethyl-substituted perfluorocyclohexane monomers has been reported (A. M. Hynes et al., Macromolecules, 1996, 29, 18-21).

A process in which textiles are subjected to plasma
15 discharge in the presence of an inert gas and subsequently exposed to an F-containing acrylic monomer is described in SU-1158-634. A similar process for the deposition of a fluoroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

20 Co-pending patent applications based upon British Patent Application Nos. 9712338.4 and 9720078.6 describe and claim a improved method of producing polymer coatings which are water and/or oil repellent on surfaces. That application
25 describes a method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising certain monomeric unsaturated organic compound which comprises an optionally substituted hydrocarbon group wherein any optional substituents are
30 halogen; so as to form an oil or water repellent coating on said substrate.

The applicants have found however that the durability of such coatings can be improved.

According to the present invention there is provided a
5 method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising one or more organic monomeric compounds, at least one of which comprises two double bonds, so as to form a layer of cross-linked polymer on said surface.

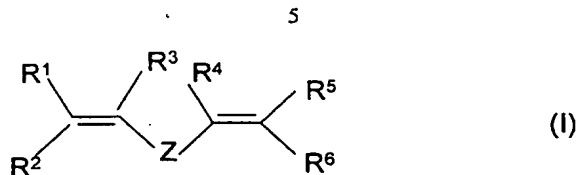
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Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by radiofrequencies (Rf), microwaves or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures
15 as are known in the art.

Suitable compounds with more than one carbon-carbon double bond, or mixtures of such compounds with other monomeric organic compounds used in the plasma are suitably those
20 which will yield cross-linked polymers having oil or water repellent properties. For water repellency, the presence of long chain hydrocarbon chains for example, alkyl chains is desirable. For oil-repellency or for water and oil repellency, the presence of haloalkyl chains, in particular
25 perhaloalkyl side chains within the compound is preferable. The cross-linked polymeric coatings obtained thereby will have good durability. For example, when applied to substrates such as fabrics, the oil and/or water repellent coating would be better able to withstand washing.

30

Suitably the compound with more than one double bond comprises a compound of formula (I)

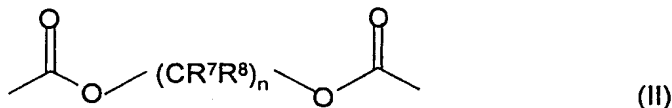


where R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 are all independently selected from hydrogen, halo, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group.

As used therein the term "halo" or "halogen" refers to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. The term "aryl" refers to aromatic cyclic groups such as phenyl or naphthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of up to 20 carbon atoms in length. The term "alkenyl" refers to straight or branched unsaturated chains suitably having from 2 to 20 carbon atoms. "Haloalkyl" refers to alkyl chains as defined above which include at least one halo substituent.

Examples of suitable bridging groups Z for use in the compound of formula (I) are those known in the polymer art. In particular they include optionally substituted alkyl groups which may be interposed with oxygen atoms. Suitable optional substituents for bridging groups Z include perhaloalkyl groups, in particular perfluoroalkyl groups.

In a particularly preferred embodiment, the bridging group Z includes one or more acyloxy or ester groups. In particular, the bridging group of formula Z is a group of sub-formula (II)

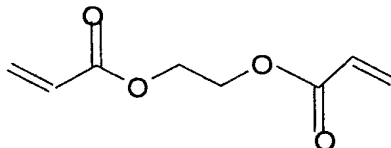


where n is an integer of from 1 to 10, suitably from 1 to 3, each R' and R'' is independently selected from hydrogen, alkyl or haloalkyl.

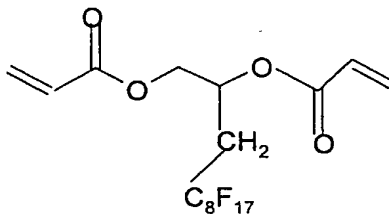
- 5 Suitably R¹, R², R³, R⁴, R⁵, and R⁶ are haloalkyl such as fluoroalkyl, or hydrogen. In particular they are all hydrogen.

Suitably the compound of formula (I) contains at least one
10 haloalkyl group, preferably a perhaloalkyl group. This allows the formation oil repellent as well as water repellent coatings. This group is suitably located as a group R' or R'' within the bridging group Z.

- 15 Thus particular examples of compounds of formula (I) include the following:



A



B

20

The compound of formula (I) is suitably mixed with another
25 monomeric compound which may also contain a haloalkyl group. This may also contain a perhaloalkyl moiety, particularly

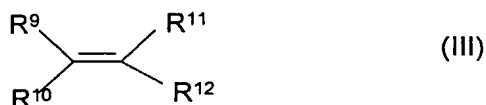
where the compound of formula (I) does not include such a group.

Where the compound of formula (I) is mixed with a further
5 compound, these may comprise unsaturated organic compounds which contain at least one double bond which is capable of reacting to form a polymeric compound.

Perhalogenated compounds, whether saturated or unsaturated,
10 may also give rise to oil and/or water repellent surfaces, particularly if they comprise long chains or rings, and these may form a further component of the plasma mixture. These compounds will suitably include perhaloalkyl or perhaloalkenyl groups having from 3 to 20, preferably from 8
15 to 12 carbon atoms.

Particularly suitable other organic compounds are those of formula (III)

20



where R^9 , R^{10} and R^{11} are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by
25 halo; and
 R^{12} is a group $\text{X}-\text{R}^{13}$ where R^{13} is an alkyl or haloalkyl group and X is a bond; a group of formula $-\text{C}(\text{O})\text{O}(\text{CH}_2)_m\text{Y}-$ where m is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(\text{O})_p\text{R}^{14}(\text{O})_q(\text{CH}_2)_t-$ where R^{14} is
30 aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0.

Preferably at least one of R^9 , R^{10} or R^{11} is hydrogen.

Suitable haloalkyl groups for R^9 , R^{10} , R^{11} and R^{13} are
5 fluoroalkyl groups. The alkyl chains may be straight or
branched and may include cyclic moieties.

For R^{13} , the alkyl chains suitably comprise 2 or more carbon
atoms, suitably from 2-20 carbon atoms and preferably from 6
10 to 12 carbon atoms.

For R^9 , R^{10} and R^{11} , alkyl chains are generally preferred to
have from 1 to 6 carbon atoms.

15 Preferably R^{13} is a haloalkyl, and more preferably a
perhaloalkyl group, particularly a perfluoroalkyl group of
formula C_sF_{2s+1} where s is an integer of 1 or more, suitably
from 1-20, and preferably from 6-12 such as 8 or 10.

20 Suitable alkyl groups for R^9 , R^{10} and R^{11} have from 1 to 6
carbon atoms.

Preferably however, at least one of R^9 , R^{10} and R^{11} is
hydrogen and preferably R^9 , R^{10} , R^{11} are all hydrogen.

25

Where X is a group $-C(O)O(CH_2)_mY-$, m is an integer which
provides a suitable spacer group. In particular, m is from
1 to 5, preferably about 2.

30 Suitable sulphonamide groups for Y include those of formula
 $-N(R^{14})SO_2-$ where R^{14} is hydrogen or alkyl such as C_{1-4} alkyl,
in particular methyl or ethyl.

In a preferred embodiment, the compound of formula (III) is a compound of formula (IV)

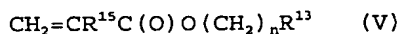


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where R^{13} is as defined above in relation to formula (III).

In compounds of formula (II), X in formula (III) is a bond.

10 In an alternative preferred embodiment, the compound of formula (III) is an acrylate of formula (V)



15 where m and R^{13} as defined above in relation to formula (III) and R^{15} is hydrogen or C_{1-6} alkyl, such as methyl.

Using these compounds, coatings with water hydrophobicity and oleophobicity values can be produced.

20

Other compounds of formula (III) are styrene derivatives as are well known in the polymer art.

All compounds of formulae (I) and (III) are either known
25 compounds or they can be prepared from known compounds using conventional methods.

The surface coated in accordance with the invention may be of any solid substrate, such as fabric, metal, glass,
30 ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which oil- and/or water-repellency is to be applied. Alternatatively, the fabric may be a synthetic fabric such as an acrylic/nylon fabric.

The fabric may be untreated or it may have been subjected to earlier treatments. For example, treatment in accordance with the invention can enhance the water repellency and
5 confer a good oil-repellent finish onto fabric which already has a silicone finish which is water repellent only.

Precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon
10 factors such as the nature of the polymer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of the plasma compound or compounds at pressures of from 0.01 to 10
15 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

20 The applied fields are suitably of average power of up to 50W. Suitable conditions include pulsed or continuous fields, but are preferably pulsed fields. The pulses are applied in a sequence which yields very low average powers, for example in a sequence in which the power is on for 20 μ s
25 and off for from 10000 μ s to 20000 μ s.

The fields are suitably applied from 30 seconds to 20 minutes, preferably from 2 to 15 minutes, depending upon the nature of the compounds used in the plasma chamber and the
30 substrate etc.

Plasma polymerisation of compounds in accordance with the invention, particularly at low average powers may result in the deposition of highly fluorinated coatings which exhibit

super-hydrophobicity. In addition, a high level of structural retention of the compound occurs in the coating layer, which may be attributed to the direct polymerisation of the particular alkene monomers for instance a
5 fluoroalkene monomer via its highly susceptible double bond.

Suitably, low power pulsed plasma polymerisation is used in order to produce well-adhered coatings which exhibit excellent water and oil repellency. This method leads to a
10 greater level of structural retention, which can be attributed to free radical polymerisation occurring during the duty cycle off-time and less fragmentation during the on-time.

15 When the plasma compounds include a perfluoroalkylated tail or moiety, the process of the invention may have oleophobic as well as hydrophobic surface properties.

Thus the invention further provides a hydrophobic or
20 oleophobic substrate which comprises a substrate comprising a coating of a haloalkyl polymer which has been applied by the method described above. In particular, the substrates are fabrics but they may be solid materials such as biomedical devices.

25 Conventional plasma deposition apparatus, as is known in the art, can be used in the method of the present application.

Claims

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- 15

- 20

- 25



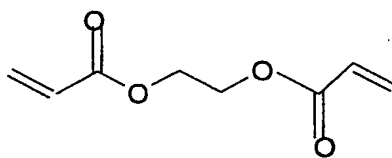
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5. A method according to any one of claims 2 to 4 wherein the compound of formula (I) contains at least one haloalkyl group.

6. A method according to claim 5 wherein the haloalkyl group is a perhaloalkyl group.

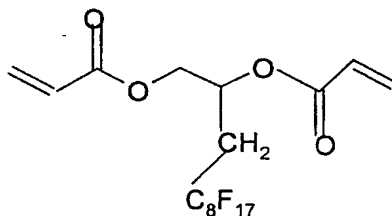
7. A method according to any one of claims 2 to 6 wherein the compound of formula (II) is

10



A.

or

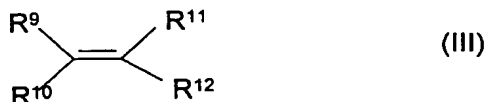


B

8. A method according to any one of claims 2 to 7 wherein the compound of formula (I) is mixed with a further monomeric compound.

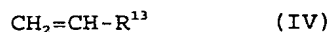
9. A method according to claim 8 wherein said further monomeric compound comprises an unsaturated organic compounds which contain at least one double bond which is capable of reacting to form a polymeric compound, or a perhalogenated compound.

10. A method according to claim 9 wherein said further organic compound is a compound of formula (III)



- where R^9 , R^{10} and R^{11} are independently selected from
 5 hydrogen, alkyl, haloalkyl or aryl optionally substituted by
 halo; and
 R^{12} is a group $\text{X}-\text{R}^{13}$ where R^{13} is an alkyl or haloalkyl group
 and X is a bond; a group of formula $-\text{C}(\text{O})\text{O}(\text{CH}_2)_m\text{Y}-$ where m
 is an integer of from 1 to 10 and Y is a bond or a
 10 sulphonamide group; or a group $-(\text{O})_p\text{R}^{14}(\text{O})_q(\text{CH}_2)_t-$ where R^{14} is
 aryl optionally substituted by halo, p is 0 or 1, q is 0 or
 1 and t is 0 or an integer of from 1 to 10, provided that
 where q is 1, t is other than 0.

- 15 11. A method according to claim 10 wherein the compound of
 formula (III) is a compound of formula (IV)



- 20 where R^{13} is as defined in claim 10.

12. A method according to claim 10 wherein the compound of
 formula (III) is an acrylate of formula (V)



where m and R^{13} as defined in claim 10 and R^{15} is hydrogen or
 C_{1-6} alkyl, such as methyl.

- 30 13. A substrate having a polymeric coating applied by a
 method according to any one of the preceding claims.

14.. A substrate according to claim 13 which is a fabric.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/01754

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06M14/18

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 120 316 A (MCNEELY) 3 October 1984 (1984-10-03) page 6, line 21 -page 24, last line ----	1-14
Y	EP 0 049 884 A (HATTORI ET AL.) 21 April 1982 (1982-04-21) cited in the application claims page 12 - page 16 : Tables -----	1-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PT/GB 99/01754

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 120316 A	03-10-1984	ES 530104 A	01-04-1986
		JP 59168178 A	21-09-1984
EP 49884 A	21-04-1982	JP 1596594 C	27-12-1990
		JP 2022370 B	18-05-1990
		JP 58005734 A	13-01-1983
		JP 1596595 C	27-12-1990
		JP 2022371 B	18-05-1990
		JP 58005735 A	13-01-1983
		JP 57089753 A	04-06-1982
		US 4382985 A	10-05-1983
		US 4421842 A	20-12-1983
		US 4421843 A	20-12-1983

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